

NANOSTRUCTURAL ASPECTS OF WEAR IN ION-BEAM DEPOSITED Pb-Mo-S FILMS

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ABSTRACT

Microstructural aspects of wear resistance have been investigated using cross-sectional transmission electron microscopy (TEM) to analyze both as-deposited and worn films. As-deposited Pb-Mo-S films were virtually amorphous, i.e., show no long range structure. Wear tracks revealed a two-part wear process localized at the sliding surface. First, Pb-Mo-S at the sliding surface was transformed into basal-oriented, crystalline MoS₂ from 1 to 4 monolayers thick. Then, as sliding continued, the MoS₂ layers were detached one or two layers at a time. Evidence for the nanometer scale wear process is presented.

INTRODUCTION

Ion-beam deposited MoS₂ films can provide ultralow friction and high endurance in sliding contacts [1]. The addition of Pb during deposition produces amorphous films whose endurance exceeds that of MoS₂ while providing equivalent friction coefficients [2]. Raman analysis suggests that crystalline MoS₂ is formed during sliding against these [2] and PbO-alloyed MoS₂ films [3], accounting for the low friction, but how and where this transformation occurs is unclear. Additionally, the Pb-Mo-S films are remarkably wear resistant [4]; how the transformation to MoS₂ influences the Pb-Mo-S film wear is not known. The purpose of this study is to demonstrate a nanometer scale understanding of this transformation and its role in the wear of Pb-Mo-S films.

EXPERIMENTAL

Pb-Mo-S films were deposited to a thickness of 200 nm on Si (100) substrates using ion beam deposition under conditions known to produce amorphous films with Pb doping concentrations of ~10-15 at.% [2, 5].

Reciprocating sliding tests were conducted in dry air with relative humidity less than 1 %. Tests were performed using 6.35 mm diameter 52100 steel balls for 100 and 1000 cycles. An applied load of 1 kgf was used, resulting in a mean Hertzian pressure 0.82 GPa and tracks ~120 μm wide. For cross-section transmission electron microscopy (TEM) observations, 10 overlapping wear tracks, spaced 100 μm apart, were made to produce a single wide track 1 mm in width. Micro-Raman spectroscopy was performed on as-deposited films, wear tracks and ball transfer films using a Renishaw imaging microscope equipped with a low-power Ar⁺ laser (514 nm); spectrometer resolution was 1 cm^{-1} and imaging resolution ~2 μm .

Cross-section transmission electron microscopy samples were made from wear tracks and as deposited films using standard techniques. Each sample was cleaved normal to the film plane; the film surfaces were glued together with a two-part epoxy, then mechanically thinned, dimpled

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and ion milled with 5.5 keV Ar^+ ions until perforation. Orientation of cross-sectioned samples was either perpendicular (across the track width) or parallel (along the sliding direction to the sliding direction). Samples were examined using a Hitachi H-9000 transmission electron microscope operated at 300 keV in imaging and selected area electron diffraction (SAED) modes. High resolution transmission electron (HRTEM) images were taken using no objective aperture.

RESULTS

Figure 1 shows micro-Raman spectra of the as-deposited film, a 1000 cycle wear track and ball transfer films after 100 and 1000 cycles. The spectrum from the as-deposited film was featureless. The 1000 cycle track shows bands consistent with those of crystalline MoS_2 (molybdenite) [6]. Micro-Raman spectra of transfer films worn to 100 and 1000 cycles also show bands consistent with MoS_2 . No evidence of oxidation products (e.g. MoO_2 , MoO_3 , or PbMoO_4) was observed. Bands near 500 and 600 cm^{-1} in the 100 cycle ball spectra are consistent with iron oxide (Fe_2O_3).

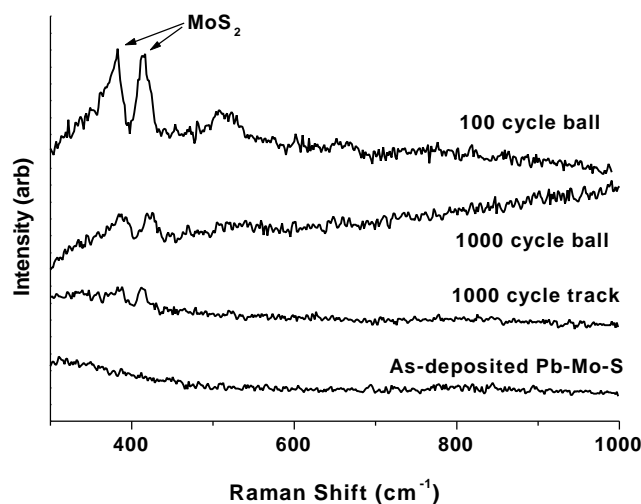


Figure 1. Micro-Raman spectra obtained from unworn Pb-Mo-S film as well as 1000 cycle wear track and ball surfaces.

Figure 2 is a HRTEM image of an as-deposited Pb-Mo-S film. The film was dense and uniform in appearance throughout and produced amorphous SAED diffraction patterns (not shown), consistent with earlier x-ray diffraction results [2]. Closer examination of Fig. 2 shows fine fringes which indicate that the films were not truly amorphous but consisted of small clusters with short range order.

Figure 3 is a HRTEM image of a 100 cycle Pb-Mo-S wear track; the sliding direction is perpendicular to the plane of the image. The interface between the lighter epoxy region (upper half) and darker Pb-Mo-S (lower half) is the wear track surface. The image clearly shows that the microstructure of Pb-Mo-S in the bulk of the film remained unchanged, i.e., amorphous after 100 sliding cycles. Horizontal fringes ~ 5 -10 nm long were observed at the wear track surface; an example is marked in the image between arrows. The spacing between fringes for this patch is ~ 0.65 nm; fringe spacing of other patches ranged up to 0.70 nm.

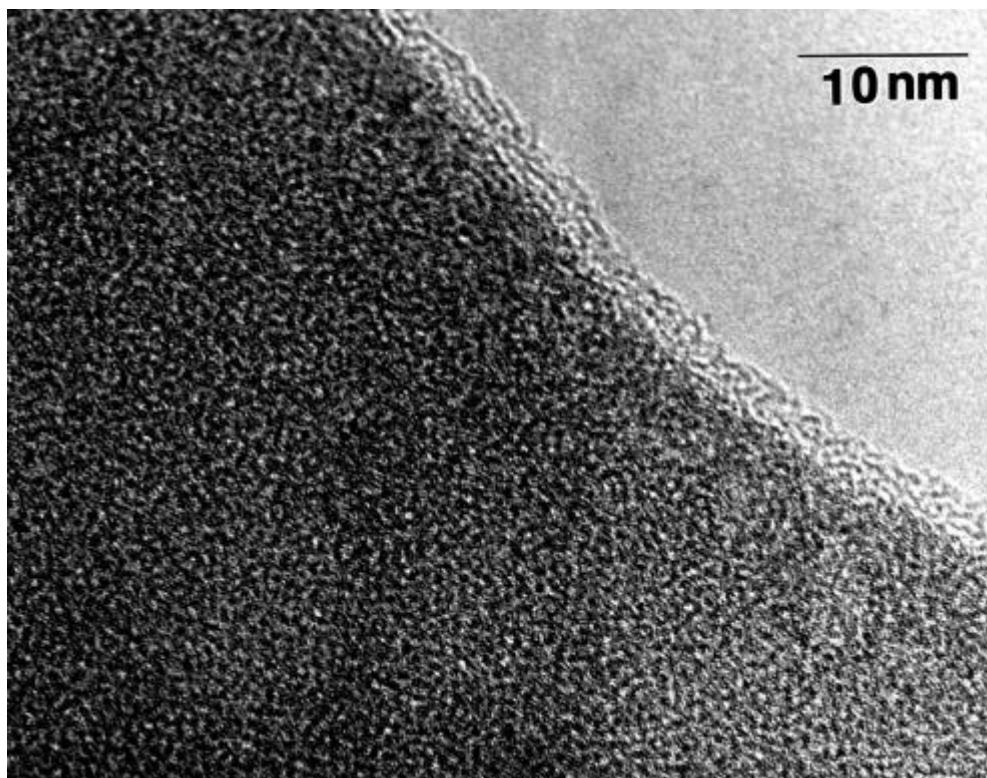


Figure 2. A HRTEM image of a cross-sectioned as-deposited Pb-Mo-S film. This film is dense and uniform with an amorphous SAED pattern (not shown). Closer examination shows that this film is not truly amorphous but appears to consist of small clusters with short range order.

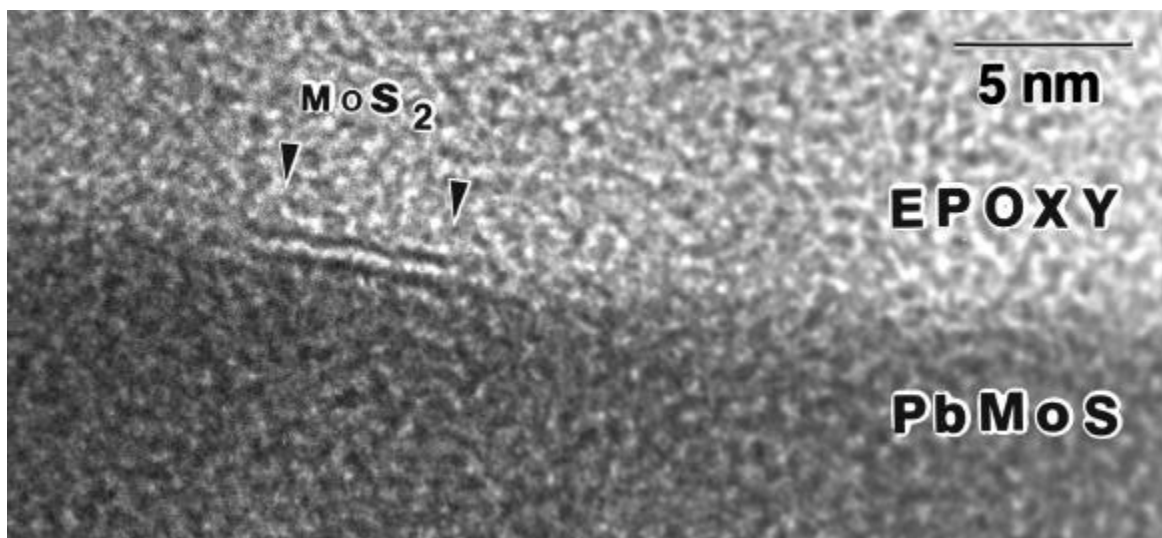


Figure 3. HRTEM image of a cross-sectioned 100 cycle Pb-Mo-S wear track. The sliding direction was along the epoxy - Pb-Mo-S interface, normal to the image plane. The Pb-Mo-S film remains largely unchanged except for small patches of transformed MoS_2 at the sliding interface (marked by arrows).

Figure 4 is a HRTEM image of a portion of the Pb-Mo-S track after 1000 cycles; the sliding direction, in this case, is parallel to the image plane. At the track surface is a crystalline

layer, 2 to 4 fringes thick; arrows mark an area where a segment of the layer has been pulled away from the surface. In addition, fringes $\sim 3\text{-}5$ nm long can be seen below the sliding surface and are marked by the letter “s”. Otherwise, the subsurface Pb-Mo-S remained amorphous.

Figure 5 is a HRTEM image taken from a different portion of the same 1000 cycle track. Three distinct regions are observed: a crystalline layer on top of the track, approximately 10-12 nm thick, consisting of nano-crystallites 3-5 nm in size; a thin, crystalline layer at the track surface, consisting of nearly continuous, horizontal fringes (typically 2 to 4 fringes thick) with a spacing of ~ 0.7 nm (as in Fig. 4) and finer vertical fringes through the horizontal fringes with a spacing of 0.27 nm; and amorphous subsurface Pb-Mo-S.

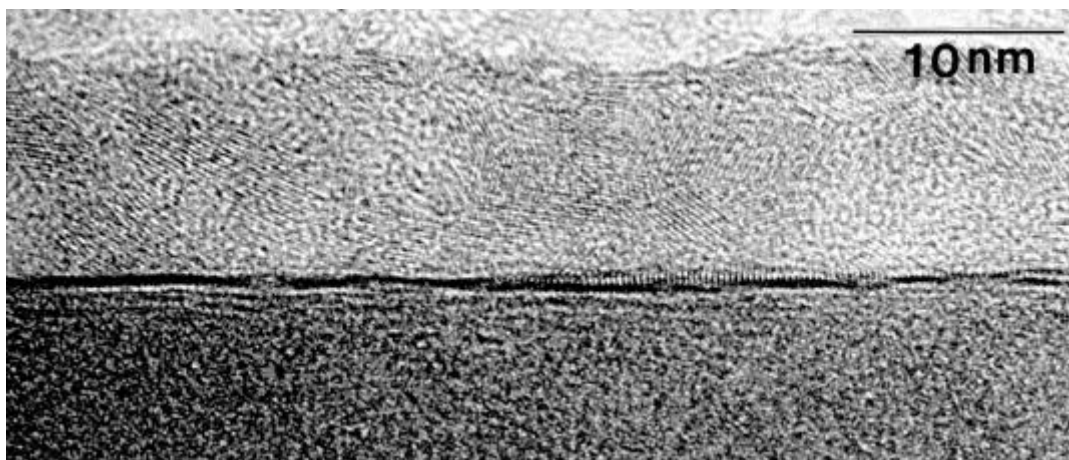


Figure 4. HRTEM image of a cross-sectioned 1000 cycle Pb-Mo-S wear track. The sliding direction is along the interface parallel to the image plane. Heavy horizontal fringes can be seen along the track surface having lattice spacings ranging from 0.65-0.70 nm, consistent with the basal plane spacing of MoS_2 . To the left and marked by arrows is a region where two basal planes have been pulled up. In addition, subsurface patches of MoS_2 can be seen in this image and are marked by the letter “s”.

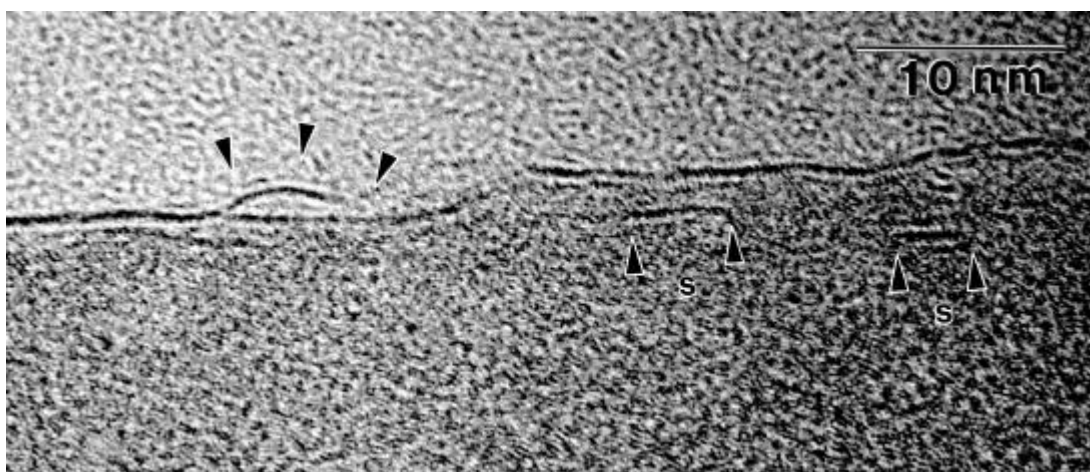


Figure 5. HRTEM image of a cross-sectioned 1000 cycle Pb-Mo-S wear track, with the sliding direction parallel to the image plane.

DISCUSSION

HRTEM of Pb-Mo-S films and wear tracks revealed three structures. First, as-deposited Pb-Mo-S films showed no long-range order and, therefore, can be considered amorphous; we leave for future consideration the significance of the fine fringes in images like Figure 2, which imply that the film has short range order within nanoclusters.

Secondly, the outermost layers of the track were crystallized by the sliding action of the steel ball. At first, only patches 1-2 nm thick were formed (e.g. Fig. 3). By 1000 cycles (Fig. 4), continuous strips, 2 to 4 layers thick, developed on the surface and small patches nucleated below the sliding surface; but in all cases, crystallization was confined to the top few nm of the sliding surface. The layers exhibited horizontal and vertical fringe spacings similar to the (002) and (100) spacings of molybdenite [7]. The (002) spacing, 0.65 - 0.70 nm, is somewhat greater than that of molybdenite (0.615 nm), but is consistent with the spacings found in MoS₂ films deposited by rf-sputtering [8] and ion-beam assisted deposition (IBAD) [9, 10]. The layers, then, are consistent with basal-oriented MoS₂.

The third structure was the crystalline material found on top of the wear track (Fig. 5). The area of this ~10 nm thick nano-crystalline layer was too small to obtain a diffraction pattern; however lattice fringes give spacings of 0.25 to 0.26 nm. These spacings were compared to those calculated for MoS₂ as well as compounds which might reasonably be expected to form (e.g. oxides and sulfides of Mo, Pb, and Fe). The lattice spacings are consistent with both the (102) orientation of MoS₂ as well as the (111) orientation of MoO₃; as we will discuss below, it is more likely that this material is MoS₂.

One wear mechanism discernable from HRTEM images is detachment of the top layer of the transformation-crystallized MoS₂. In Figure 4, areas along the sliding surface were observed where one or two basal planes detached from the transformed layer. This provides the first direct evidence that wear of MoS₂ films can occur by layer-by-layer detachment. This wear mode can be accounted for by the weak Van der Waals bonding between MoS₂ layers, a property which has also been used to explain the low shear strength of MoS₂ [11]. Additionally, this wear mode might account for the very low (sub-nanometer per cycle) wear rates of Pb-Mo-S films [4].

Detached basal planes of MoS₂ could have been reoriented and pressed back onto the surface. Alternatively, they could have attached to the steel ball and collected as transfer film, which according to Raman data (Fig. 1) contained MoS₂. Some of this transfer film could have been redeposited as debris on the track, which would account for the material seen on top of the 1000 cycle track (Fig. 5). The debris is likely MoS₂ (and not MoO₃), since MoO₃ was not detected in the Raman spectra of the 1000 cycle track or the 100 and 1000 cycle transfer films, despite having a hundred-fold larger Raman scattering cross-section than MoS₂ [3]. If the debris were indeed MoS₂, then it is worth noting that it was not redeposited with the basal orientation aligned parallel to the sliding direction.

The data presented here suggest that wear of Pb-Mo-S occurred in several stages. First, sliding nucleated small patches of basal-oriented MoS₂, which later grew into continuous, thin layers of MoS₂ on the track surface. Then, single layers of MoS₂ were detached, one or two at a time. Concurrently, bits of layers transferred to the ball and later reattached to the track surface. The identification of the crystalline debris and its subsequent role in the wear or wear-resistance of Pb-Mo-S are left to future investigations.

SUMMARY AND CONCLUSIONS

Ion-beam deposited Pb-Mo-S films were shown by HRTEM to be amorphous. Sliding transformed surface layers to crystalline, but basal-oriented MoS₂. A wear mode of Pb-Mo-S films was inferred from HRTEM of transverse cross-sections of wear tracks and from Raman spectra of tracks and ball transfer films. First, individual layers of crystallized MoS₂ detached from the surface. Second, the layers collected as transfer film on the ball and later as MoS₂ debris on the track.

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